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OF WASTES TO MITIGATE THE REACTOR CORROSION PROBLEM.

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A FLOW REACTOR FOR THE SUPERCRITICAL WATER OXIDATION OF WASTES TO MITIGATE THE REACTOR CORROSION PROBLEM.

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ABSTRACT.

We have designed a flow tube reactor for supercritical water oxidation of wastes that confines the oxidation reaction to the vicinity of the axis of the tube. This prevents high temperatures and reactants as well as reaction products from coming in intimate contact with reactor walls. This implies a lessening of corrosion of the walls of the reactor.

We display numerical simulations for a vertical reactor with conservative design parameters that illustrate our concept. We performed our calculations for the destruction of sodium nitrate by ammonium hydroxide in the presence of supercritical water, where the production of sodium hydroxide causes corrosion. We have compared these results with that for a horizontal set-up where the sodium hydroxide created during the reaction ends up on the floor of the tube, implying a higher probability of corrosion.

I. Introduction.

Oxidation in supercritical water is the method of choice for the elimination of a variety of wastes.[1] One of the major concerns in designing a reactor for the supercritical water oxidation of wastes is the corrosion that occurs on the reactor walls, seriously shortening the lifetime of the reactor.[2] Given the wide array of wastes, ranging from organics to fuel propellants, that can be treated with this process, it is clearly desirable to lessen or eliminate the corrosion problem in order to enhance its usefulness.

Corrosion of reactor walls is usually caused during the destruction of inorganic wastes.[2] For example, during the destruction of nitrates, sodium nitrate in particular,[3] it is believed that sodium hydroxide is formed, and eats away at reactor walls. In practice, it is found that having the oxidizer-supercritical water mixture in contact with the walls is a less serious problem than having the waste stream and reaction products in contact with the walls. The reason for this is that the walls can be passivated by electrochemical means against corrosion from the oxidizing stream.

There are a variety of ways of dealing with the wall corrosion problem. In the case of gas turbine engines, special coatings are used.[4] Alloy coatings are sometimes applied to prevent corrosion in the hot stages of turbine engines.[5]

Clearly, the simplest way to deal with the problem in tube reactors is to prevent the waste stream and the reaction products from ever reaching the walls. With this in mind, we can think of a vertical tubular flow reactor. In this reactor, a mixture of supercritical water and sodium nitrate (a few percent by weight) is fed in through an inlet tube at a predetermined rate e.g. 1500 gallons per day. This corresponds to a flow velocity of about 20 cm/s in an inlet tube about 1cm in radius. The waste stream is introduced along the axis of the tube. Preheaters on the inlet tube cause the mixture to be heated to a temperature close to the wall temperature of the reactor, so that convection currents due to gravity are minimized. If the tube is long enough to allow the reaction to proceed to completion, and if the tube is sufficiently wide to prevent the mixed reacting stream from coming in contact with the walls before it leaves the tube, then we will have solved the corrosion problem. Practical considerations may force us to use tubes smaller than the optimal

size, In which case there may be some contact between the corrosive reaction product and the walls. In this scenario, the Inlet tube Is sacrificed to corrosion, since it comes In intimate contact with the reactants near operatlng conditions. Further downstream, the reaction products have to be collected for separation, and so one again must appeal to an annular chamber (within the main reaction chamber) which will be considered to be sacrificial, for the sake of preventing corrosion of the outer reaction chamber.

In this paper we have used KIVA-3,[6] a Continuum Fluid Dynamics (CFD) code for simulating low-speed reactive flows to model such a reactor. Since we wish to display the basic principle behind our idea, we will display results for only a section of our vertical reactor, and will not simulate the presence of details such as the annular collection chamber we described above. The generic KIVA-3 code was modified by us to handle equations of state for non-ideal gases, of which supercritical water Is definitely an example, at a pressure of about 300 bars, and temperatures of about 800K. The modification was carried out by the use of the compressibility factor In the equation of state, which expresses deviation from an ideal gas law.

II. Numerical calculations.

As mentioned In the previous section, the idea Is to shape the reacting flow In our reactor such that It does not touch the walls, or at least touches the walls minimally, in order to minimize, if not avoid, corrosion completely. The physical picture we have is that of a narrow jet issuing Into the center of a cylindrical tube, flowing downstream while spreading laterally In a plume, as the oxidizing reaction proceeds.

We have performed numerical simulations of such flows using KIVA-3,[6] which uses a semi-implicit method for advancing In time. While this code Is a state-of-the-art tool designed to primarily handle internal combustion engines, it has options for inflow and outflow boundary conditions that allow it to be utilized for our purposes. The equation of state treatment in the generic version of the code had to be modified In order to accomodate deviations from the ideal gas law. This was achieved by using the compressibility factor. Using NIST steam tables, we generated a table of $P/\rho RT$ (P Is the pressure, ρ Is the density of water, R Is the universal gas constant and T Is the temperature) as a

function of temperature at the pressure we were interested in, viz., 300 bars. The variation of $P/\rho RT$ with T was fitted to a fifth-order polynomial. This parameterization was then inserted into the code. The corresponding use of the enthalpy tables was also modified, so that the proper specific heat is obtained during calculations. The non-idealness of the steam entering the reactor tube was also accounted for properly at the inflow and outflow boundaries.

As an example of reactive flows confined to the neighborhood of the axis of the tube, we have used an aqueous solution of sodium nitrate (5% by weight) to simulate the waste stream. Ammonium hydroxide (10% by weight) was added to the incoming stream to oxidize the sodium nitrate into sodium hydroxide and other products. The data of Dell'Orco et al[3] has been fitted to a first-order reaction rate. This yields a global reaction mechanism which is easy to insert into KIVA-2. What is not clear however, is the value of the heat of reaction. The study of Dell'Orco was aimed at gathering data on the destruction rate, and while they did obtain some data on the reaction products, it is not sufficient to determine the heat of reaction. What is clear from the experiments however, is that the overall reaction is neither terribly endothermic nor exothermic. In any event, we are considering fairly dilute solutions, so that it may be fair to assume that the heat of reaction is of no consequence to the modeling study. The simple approach we then followed was to assume that:

$$NaNO_3 + NH_4OH \rightarrow NaOH + NH_4NO_3;$$

$$(2.1)$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$
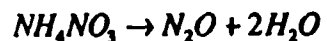
The heats of formation of the individual molecules are readily available and suggest that the overall scheme is slightly exothermic.

Our main concern is the distribution of NaOH within the reactor, since it is believed that it is the main cause of reactor corrosion in this method of oxidation. We have therefore elected to use the following global reaction:

$$NaNO_3 + NH_4OH \rightarrow NaOH + NH_4NO_3 \qquad (2.2)$$

where the heat of reaction (123.9kcal/mole) is that obtained for Eqn.(2.1) above.

The reaction rate was given by Dell'Orco et al:[3]

$$\frac{d[NaNO_3]}{dt} = -A \exp\left(-\frac{E_a}{RT}\right)[NaNO_3][NH_4OH] \tag{2.3}$$

where $A = 2.04 \times 10^{22}$ (mol/L)/s, $E_a = 298$ kJ/mol, in the temperature range 450-550°C.

The simulations were performed for a tube 5cm (diameter) x 20cm (length). In this tube we have a simulated an inlet tube with an entrance hole about 1cm in radius at the top of the flow reactor. The bottom of the reactor is left fully open. Gravity was assumed to drive the flow from the top down. The procedure we followed was to start a flow of supercritical water loaded with a 5% solution of sodium nitrate and 10% ammonium hydroxide going into our reactor at 20cm/s (corresponding approximately to 1500 gallons per day). The grid was assumed to be three-dimensional, since we wanted to compare this run with the reactor held horizontal. As discussed in the previous section, the boundary layer that develops is too small to be numerically resolved and we performed the simulations with free-slip boundary conditions.

As the flow proceeds downstream the reaction given by Eqn.(2.3) takes place. Since we have chosen to perform the simulations with a relatively short tube, and the flow velocity is relatively high (high Damkohler number) the heat produced in the reactive flow is not sufficient to cause much difference to the local temperature. We display our results about 2s into the run. The code ran for just under 12 hours on an HP 735 to obtain these high resolution results. The number of cells in the x-y-z directions were 20x30x20. Figure (1) shows contour plots of the concentration of the NaOH in the tube. The main result obtained from these calculations (Fig. 1) is that the distribution of sodium hydroxide is confined mainly to the neighborhood of the axis, thereby lessening corrosion of the walls.

We must remind the reader that the radius of the tube and also the inlet hole were chosen in a conservative manner, so as to provide only a moderate

decrease of NaOH at the walls. Much better results could be obtained by both increasing the width of the tube and decreasing the radius of the inlet hole.

Even with this conservative design of the reactor, the results are very good, compared to the operation of the reactor when placed horizontally on its side, rather than vertically. We have displayed in Fig.(2) the results of such a calculation. The temperature difference between the incoming stream and the reactor walls when combined with gravity set up convection currents. This causes the reactants to spend much more time in the reactor than in the vertical case. While this makes for a shorter reactor tube, it also means that the reaction product, viz. NaOH comes into intimate contact with the walls. Indeed, the sodium hydroxide basically splashes onto the floor of the horizontal reactor, as shown in Fig. 2. Clearly this must lead to greater corrosion of the walls than the vertical asembly we discussed above. For this simulation, the k-ε turbulence model[6] was turned on, since the high Reynolds number ($\sim 10^4$), and the complicated convection patterns suggest that the flow in this case is turbulent.

Returning to the vertical set-up, we note that optimization calculations will be necessary to determine the smallest possible tube diameter one can use for a giver set of operating conditions.

In this paper we have suggested the use of tubes that are much larger than the ones currently used in flow reactors for supercritical water oxidation.[7] We have found it necessary to use such dimensions in order to eliminate corrosion of walls. While at first sight such dimensions might sound rather exorbitant, we point out that one would necessarily have to go to such dimensions in order to process large amounts of waste. In fact, we know that if we use Inconel 625 to build the reactor to operate at 15000 psi (~1kbar) and 550 C, we need a ratio of outer diameter (o.d.) to inner diameter (i.d.) of about 2.[8] Thus, for an i.d. of 5cm, we would need an o.d. of 10cm, i.e. a wall thickness of 2.5cm.

IV. Conclusion.

We have designed a vertical flow reactor that reduces the risk of wall corrosion by shaping the low-speed reactive flow such that it stays away from the walls of the reactor. Comparison of this geometry with operation in the

horizontal mode clearly shows the advantage of our simple concept. As pointed out in the Introduction, this scheme is not a panacea, as the inlet nozzle as well as a collection vessel have to be sacrificed (to corrosion) in the process.

V. Acknowledgements.

FIGURE CAPTIONS

Figure 1: Sodium hydroxide mass fraction (ratio of the mass of the specie to the total mass in the cell) contours 2.1s after injection begins. The reacting flow has almost reached the far end of the *vertical* tube reactor. The dimensionless mass fraction contours range from 9.32e-6 to 8.37e-5. The low value is near the walls, indicating less contact between sodium hydroxide and the walls than one might have in a tube of smaller dimensions. This imples that the corrosion of the walls will be less in this case.

Figure 2: Sodium hydroxide mass fraction contours approximately 0.7s after injection begins. for a tube that is placed *horizontally*. The contours range from 1.07e-6 to 9.59e-6. The high value of the contours occurs near the floor of the tube. Notice the intimate contact between the corrosive sodium hydroxide and the floor of the tube. Compare this figure to Fig. 2, which corresponds to the vertical reactor setup.

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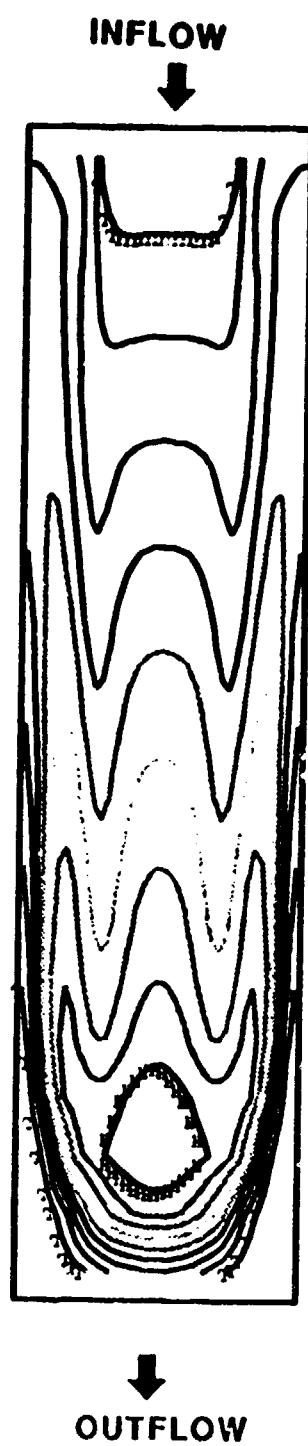
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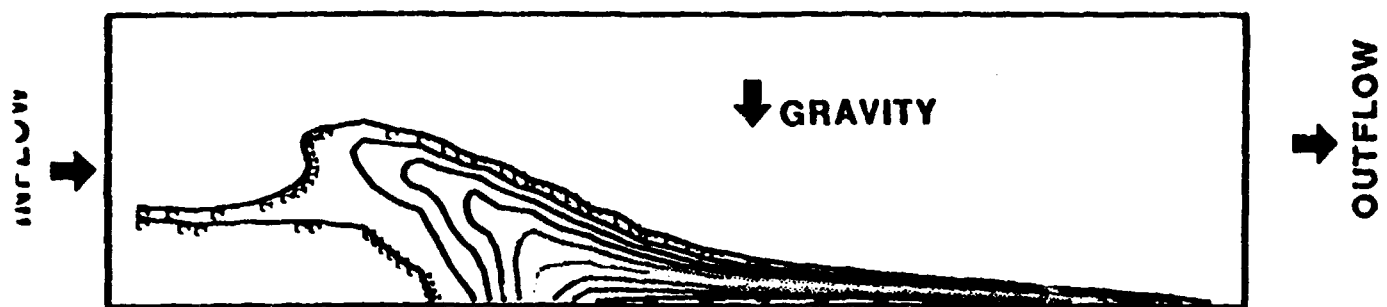
INFLOW

GRAVITY

OUTFLOW

FIGURE 1

GRAVITY

INFLOW

OUTFLOW

FIGURE 2